

Supporting Information

The Kinetics Enhancement for Lithium–Sulfur Batteries by Interlinked Hollow MoO₂ Sphere/Nitrogen Doped Graphene Composite

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Experimental Section

Preparation of MoO₂/G, MoO₂ and rGO: Graphene oxide (GO) was prepared by modified Hummers method. For the formation of MoO₂/G, the solution A was prepared by add (NH₄)₆Mo₇O₂₄·4H₂O (100 mg) into 30 mL hydrochloric acid (2 M) stirring for 30 min, and 10 mL GO (3 mg/mL) was added into the solution followed with ultrasonication for 30 min. 100 mg PVP (MW~58000) was added into 30 mL DI with stirring to form a transparent solution, then add 100 mg ascorbic acid with continue stirring as solution B. Then add solution B into solution A slowly and keep stirring for 60 min. The obtained solution was transferred into a Teflon-lined stainless steel autoclave and heated at 180°C for 48 h. The aerogel was collected by wash with DI for times and freeze dried. To remove the residuals, the aerogel was annealed at 600 °C for 4 h under Ar atmosphere. The bare hollow MoO₂ sphere was synthesized by the same method but without GO addition, and the rGO was prepared by simple hydrothermal process, GO suspension (3 mg/mL) was heated at 180 °C for 24 h. The different rGO content composites were prepared with different concentration of rGO.

Synthesis of MoO₂/G-S, MoO₂+G-S and rGO-S composites: The MoO₂/G-S compound was obtained by a simple melting-diffusion method. The MoO₂/G powder was milled with sulfur together uniformly (the mass ratio is 1 : 4) and follow with heating at 155°C for 12h in a sealed Teflon-lined stainless steel autoclave. The rGO-S compound was prepared with the same method but employ rGO powder. And the MoO₂+G-S was prepared by mixing 6 wt% rGO, 14 wt% MoO₂ and 80 wt% sulfur powder with the same melting-diffusion process. And MoO₂/G-S with different sulfur content was prepared with different mass ratio of MoO₂/G and sulfur powder.

Visualized adsorption test: A 10 mmol/L Li₂S₄ solution was prepared by adding sulfur and Li₂S at a molar ratio of 1:3 in 1, 2-dimethoxymethane/1, 3-dioxolane (DME/DOL) (1:1 by volume) solvent followed by vigorous magnetic stirring at room temperature till the solid dissolve into a uniform solution. 30 mg of MoO₂/G and rGO powders were added into 3 mL solution respectively and aged for times to observe the color of the solution.

Structure characterizations: The morphologies were characterized by scanning electron microscopy (Hitachi, SU8010) and transmission electron microscopy (Tecnai G2F30, FEI, US). X-ray diffraction (PANalytical X'Pert PRO, monochromated Cu K α radiation 40 mA, 40 kV) was used to characterize the crystal structure. Thermogravimetric analyzer system was used to analyze the sulfur and carbon contents in the compound. The specific surface area, pore volume and N₂ adsorption/desorption isotherms were measured by an ASAP 2020 (Micromeritics). X-ray photoelectron spectroscopy (Fisher Scientific Ltd, Nepean, ON) analysis was performed at room temperature to analyze the valences, compositions and contents of elements.

First-principles calculations: First-principles calculations were performed using the density functional theory with the module CASTEP (Cambridge Serial Total Package) in the Materials Studio (Accelrys Inc.,

San Diego, CA). Exchange-correlation interaction was described by Perdew-Burke-Ernzerhof in GGA (the General Gradient Approximation). A cutoff energy of 260 eV were employed for this computations. The adsorption energy is defined as the energy difference between the adsorbed complex and the adsorbent and adsorbate.

Battery assembly and measurement: The cathode were prepared by mix 80% composite materials, 10% super P and 10% PVDF by an adjustable high-speed electric agitator for 12h to obtain a homogeneous slurry. The slurry was coated onto aluminum foil uniformly, and then dried at 60 °C for 12 h under vacuum. The cathode was cut and shaped into a circular disc as a cathode. CR2025 coin cells were assembled in an argon-filled glove box, in which both the moisture and oxygen contents were controlled to be less than 1.0 ppm. The electrolyte was 1 M LiTFSI in DOL/DME (1:1 by volume) with 0.2 M LiNO₃. Lithium-metal foil was used as anode, which were separated by the Cellgard 2400 separator with the cathode. The batteries were tested on a Neware system and perform the galvanostatic cycling measurements between 1.7 and 2.8 V (vs Li⁺/Li) at room temperature.

Supplementary Figures

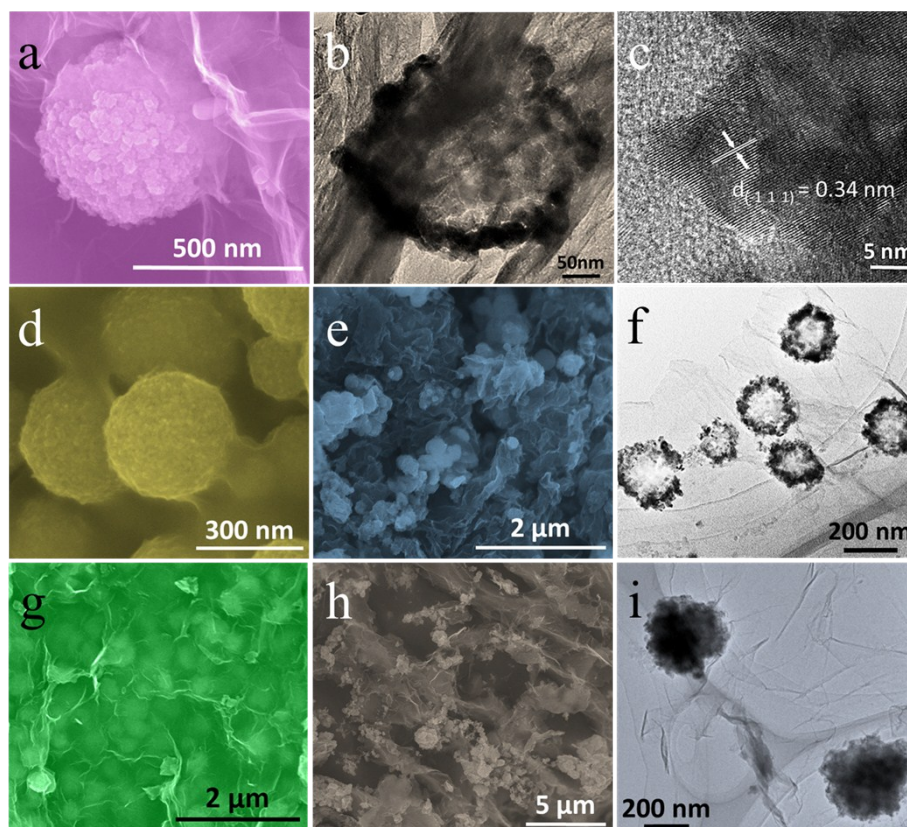


Fig. S1 Morphology and structural characterization. (a) SEM image and (b-c) TEM images of MoO₂/G. (d, e) SEM images and (f) TEM image of MoO₂+G. (g) SEM image of MoO₂/G-S. (h) SEM and (i) TEM images of MoO₂+G-S.

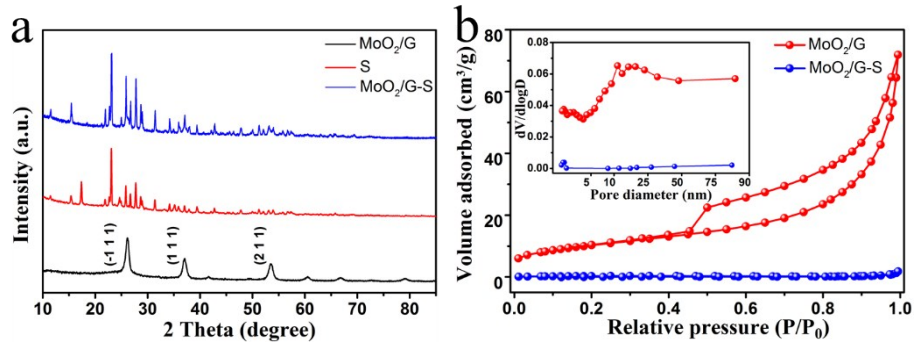


Fig. S2 (a) XRD pattern of MoO₂/G-S, MoO₂/G and S. (b) Nitrogen adsorption–desorption isotherm of MoO₂/G and rGO. Inset image shows the pore size distribution.

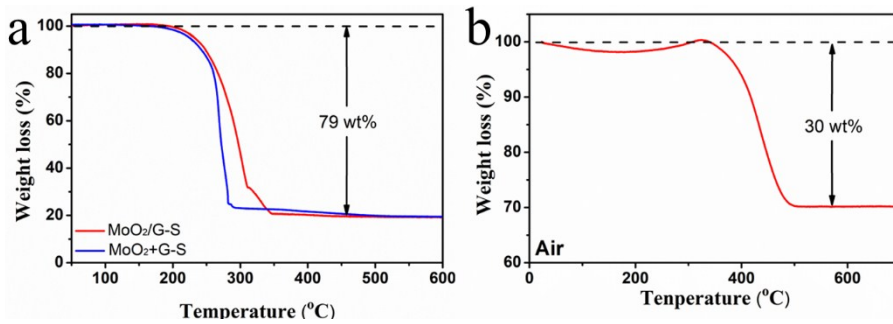


Fig. S3 TG traces of (a) MoO₂/G-S and MoO₂+G-S; (b) MoO₂/G.

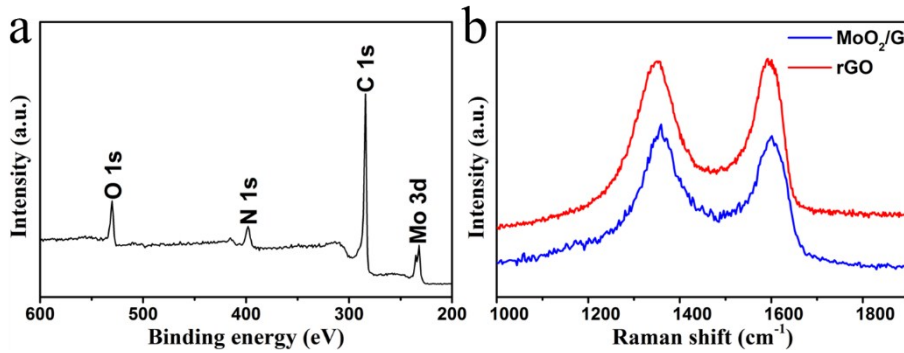


Fig. S4 (a) XPS full survey spectrum of MoO₂/G. (b) Raman spectrum of MoO₂/G.

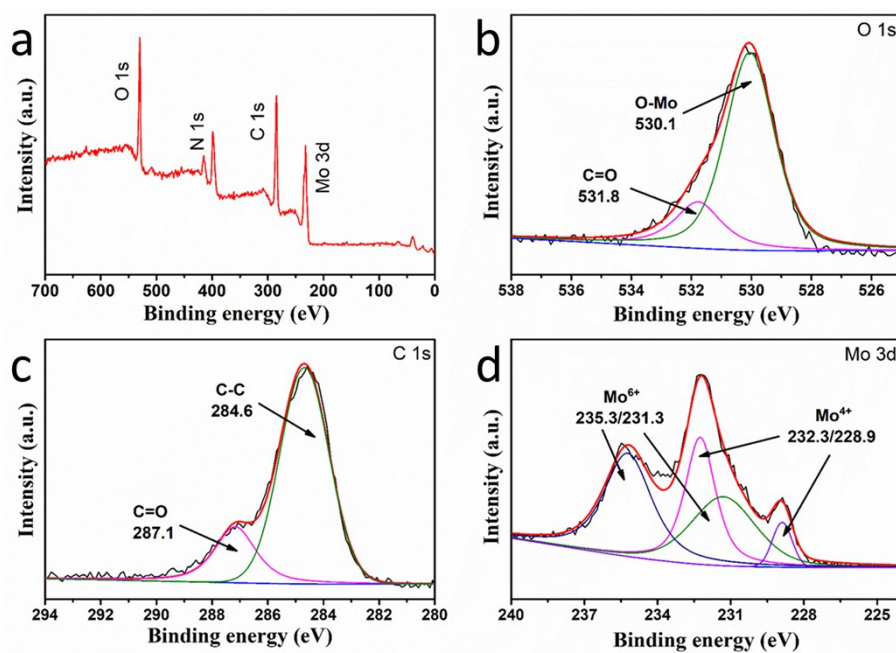


Fig. S5 XPS spectrum of MoO₂+G: (a) full survey, (b) O, (c) C and (d) Mo.

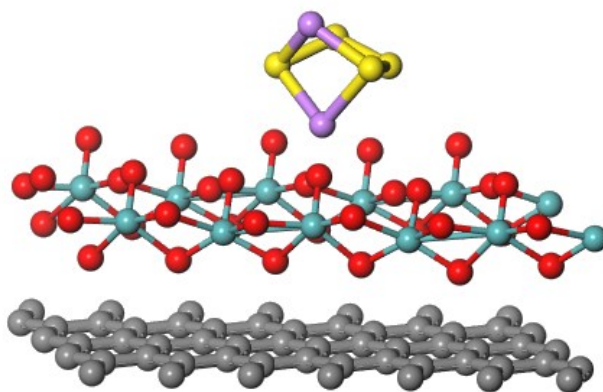


Fig. S6 Optimized structures of binding energies and geometries of the most stable Li₂S₄ on MoO₂+G.

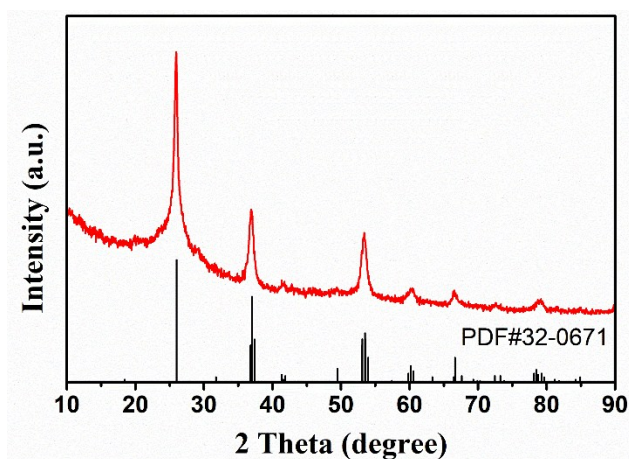


Fig. S7 XRD pattern of MoO₂/G after visualized adsorption test.

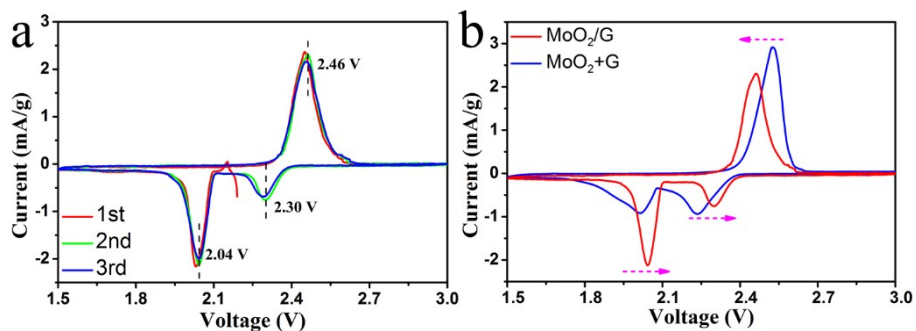


Fig. S8 CV curves of (a) MoO₂/G and (b) MoO₂/G and MoO₂+G.

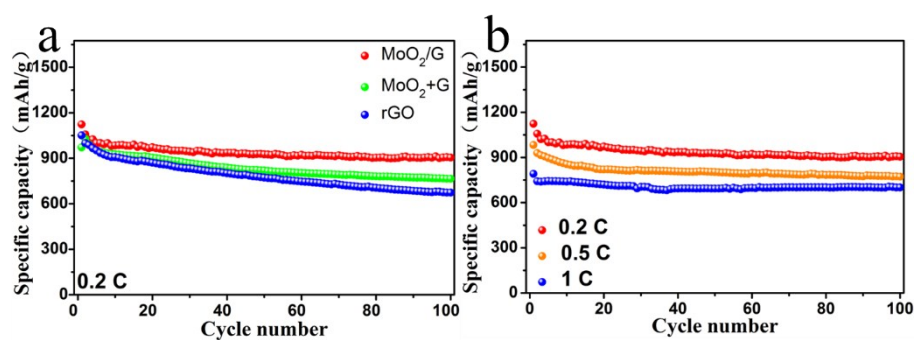


Fig. S9 (a) Cycling performance of MoO₂/G, MoO₂+G and rGO at 0.2 C. (b) Cycling performance of MoO₂/G at various rates.

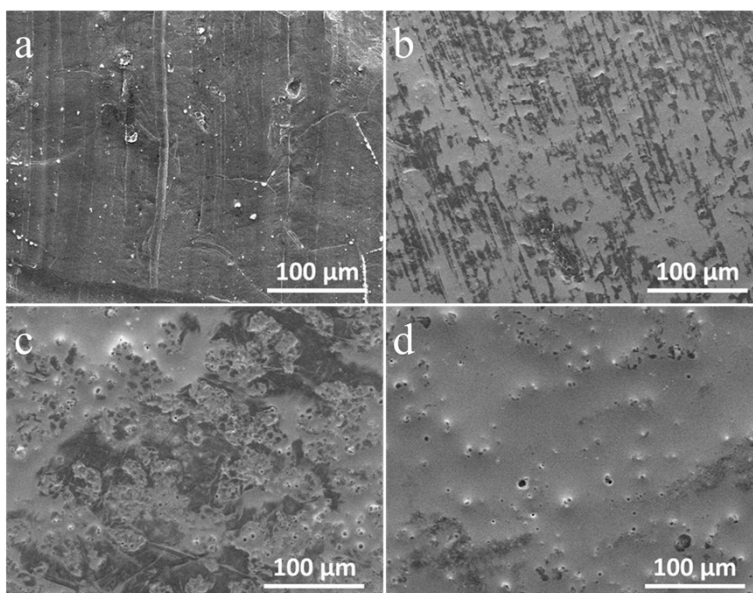


Fig. S10 SEM images of lithium: (a) fresh, (b) cycled MoO₂/G-S, (c) cycled MoO₂+G-S and (d) cycled rGO-S.

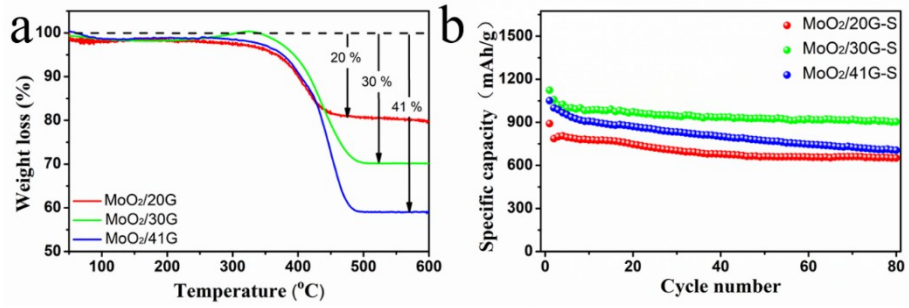


Fig. S11 (a) TGA curve of different amount of rGO in the MoO₂/G. (b) Cycling performance of different rGO content.

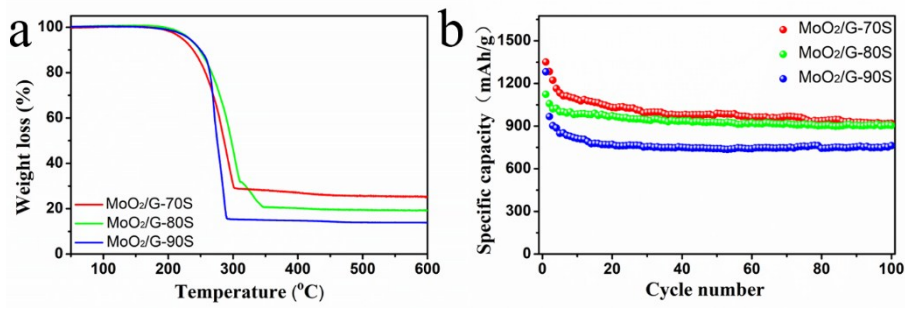


Fig. S12 (a) TGA curve of different sulfur contents. (b) Cycling performance of different sulfur contents.

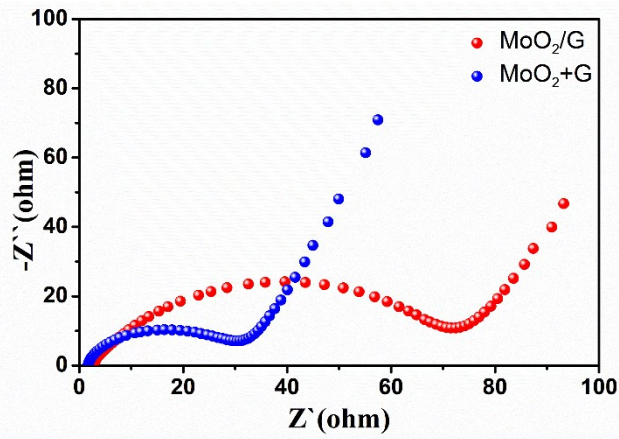


Fig. S13 (a) Electrochemical impedance spectra of cycled MoO₂/G-S and MoO₂+G-S.